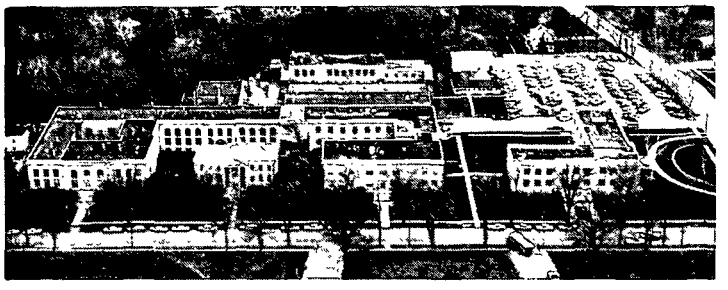

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REMOVAL OF COLOR FROM CARBONATE PULPING EFFLUENT BY THE CALCIUM–MAGNESIUM COAGULATION PROCESS

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INTRODUCTION

Color is one of several nonconventional pollutants that will probably be regulated in the future. Present color removal processes are very costly and have not been shown to be extremely reliable. A key element of this study was to determine design criteria and also to provide insight into the mechanisms involved in one proposed color removal process.

Concurrent with the uncertainty over color removal regulations and processes is the emerging situation with carbonate pulping processes. Many mills, for a variety of reasons, are converting their NSSC operations to carbonate. The implications of such a conversion to effluent color removal processes have not been fully assessed.

The objective of this study was to explore the use of the lime/magnesium color removal process for carbonate effluents and to determine if any differences in chemical composition existed between biologically treated carbonate and NSSC effluents.

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ABSTRACT

Many NSSC mills are converting to sulfurless carbonate pulping. The objective of this study was to explore the implications of such a switch to a color removal process, lime-magnesium precipitation, presently proposed for NSSC effluents. It was found that because the chemical make-up of the NSSC and carbonate effluents are significantly different, only lime is required for effective color removal.

Removal of color from carbonate pulping effluent by the calcium-magnesium coagulation process

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Introduction

Due to a variety of considerations, many neutral sulfite semichemical mills are changing their pulping process to sulfurless "carbonate" pulping. Reasons given for this switch include poor markets for NSSC liquor byproducts, high chemical costs, and sulfur emission problems (1). Since color removal from mill effluents is expected to become a concern in the near future, it was thought appropriate to explore the implications of such a switch in pulping process to proposed color removal processes. The objective of this study was to remove at least 90% of the color from a whole mill effluent by using minimum quantities of calcium and magnesium salts as the coagulating agents. The calcium-magnesium process has been successfully applied to an NSSC effluent (2), however, no prior work on carbonate effluents has been reported.

Previous work

In 1971, Black, Shuney and Fleming (3) reported that Mg^{++} is the most economical coagulant for the treatment of potable water. This encouraging report prompted NCASI to do a preliminary investigation into the possible application of this process for NSSC effluent color reduction. In their recent laboratory investigation (4), they found that 90% of the color can be removed by using lime to adjust the pH to 11.0, and then adding the appropriate Mg^{++} dosage, 100 ppm for an effluent of

2500 color units and 200 ppm for an effluent of 5000 color units. They also discovered that a substantial amount of Mg^{++} can be recovered from the sludge and effectively recycled, making the proposal practical and economically attractive.

Eidsness and Black (5) found that converting most of the insoluble $Mg(OH)_2$ to the soluble bicarbonate by bubbling CO_2 into the sludge, greatly reduces the time of settling and final volume of the settled sludge.

Black, et al. (3) suggested that not all $Mg(OH)_2$ could be removed from the sludge by carbonation, because as carbonation progresses, there will be an increasing tendency for undissolved $Mg(OH)_2$ to react with dissolved $Mg(HCO_3)_2$ resulting in the precipitation of $MgCO_3 \cdot 3H_2O$ in the carbonation tank

$$Mg(OH)_2 + Mg(HCO_3)_2 + H_2O \rightarrow 2\ MgCO_3 \cdot 3H_2O$$

Thompson, et al. (6, Part II) suggested that the solubility of $Mg(OH)_2$ under jar test conditions varied for each of the natural waters studied. Thus, it is desirable to determine the solubility relationship for each water.

Black (7) found that color was released from the magnesium sludge upon carbonation. Therefore, color bodies should be incinerated from the sludge before carbonation to avoid color release.

Laboratory scale evaluation of the lime-magnesium process by Domtar Ltd. (8) indicated that a lime dosage of 500 ppm as $Ca(OH)_2$ and 50 to

100 ppm of MgO were capable of achieving 90% color removal on a biologically treated kraft mill effluent.

Dugal, et al. (9) in detailed studies on color characterization before and after lime treatment, concluded that lime treatment was able to remove color bodies from bleach caustic extraction stage, but was not effective for NSSC effluent.

Experimental

Many methods have been employed to evaluate coagulation processes, but the jar test has been the most widely used. It was the method chosen for this study. All series of jar tests were statistically designed with the aid of a computer program in order to obtain empirical relationships between percentage color removal and calcium and magnesium dosages at various pH levels.

Jar test procedure

1. pH was adjusted to the appropriate level.

2. The required dosage of magnesium and/or calcium was added and rapid mixing at 100 rpm was provided for 2 minutes.

3. A slow mixing at 50-55 rpm was provided for an additional 20 minutes.

4. The sludge was allowed to settle for one hour and the supernatant was separated from the sludge. The supernatant was used for color measurements.

Source of carbonate effluent

The secondary effluent from a carbonate mill located in Michigan was used in this study as the principal source of effluent. It will be referred to as Mill A. The model developed for Mill A was tested by using effluent from another carbonate mill, which will be referred to as Mill B. Both mills pulp primarily mixed northern hardwoods.

Color measurement

All color measurements were performed in accordance with standard techniques (10). This procedure requires all samples for color measurement to be filtered through a 0.8 micron membrane filter and pH adjustment of the sample to 7.6 before measuring absorbance at a wavelength of 465 nm on a spectrophotometer.

Coagulation reagents

Reagent grade magnesium sulfate [$MgSO_4 \cdot 7H_2O$] and calcium chloride [$CaCl_2$] were used as the coagulating reagents.

When required, NaOH or HCl were used for pH adjustment.

IR spectra

IR spectra were run on a Perkin-Elmer Model 621 grating infrared spectrometer.

Results

Optimum calcium and magnesium dosage and pH level for 90% color removal

In order to obtain optimum dosages of coagulating reagents at specific pH levels, a series of jar tests were performed. These experiments revealed that an acceptable color removal can be obtained either by using 350 ppm of Ca^{++} or 350 ppm of Mg^{++} alone at a pH level of 12. It was also observed that pH plays a very significant role in precipitating color bodies; not much color removal was observed at pH below 12. In the case of this carbonate effluent, it apparently does not really matter whether Ca^{++} or Mg^{++} is used for precipitation of color bodies as long as a high pH is maintained. This is very interesting phenomenon and this observation, together with the IR spectra lends insight into the role of Mg^{++} in the color removal process. This is further discussed in the color removal mechanism section.

The regression equation developed for these sets of experimental data is:

$$Y = 65.4 + 2.11\ X_1 + 16.21\ X_2 + 40.875\ X_3 - 3.52\ (X_1X_2)$$
$$-3.10\ (X_1X_3) - 0.85\ (X_2X_3) - 14.01\ X_1^2 - 12.46\ X_2^2 - 1.137\ X_3^2$$

where

$\underline{Y}$ = % color removal

$$\underline{X}_1 = \left[\frac{\text{ppm of } Mg^{++}}{500}\right] - 1$$

$$\underline{X}_2 = \left[\frac{\text{ppm of } Ca^{++}}{500}\right] - 1$$

$$\underline{X}_3 = \frac{pH - 9.8}{2.2}$$

This equation can be used to predict the percent color removal for any given dosage of Ca^{++}, Mg^{++}, and pH level in the range of variables studied. Approximately 92% of the change in color can be explained by this equation. Figure 1 graphically represents the regression equation.

[Fig. 1 here]

Infrared spectra of effluents

The purpose of studying the IR spectra, shown in Fig. 2-4, of the untreated effluents was to gain a better understanding of the chemical nature of the effluents. It was decided to compare the carbonate spectra with an NSSC spectrum in order to ascertain important differences between carbonate and NSSC effluent composition.

[Fig. 2-4 here]

The interpretation of the spectra is given in Tables I and II.

[Tables I and II here]

The presence of lignosulfate is undesirable for color removal because it forms a salt with bivalent metals (for example, Ca-lignosulfate) and remains in the system because it is partially soluble. Less lignosulfate in the carbonate effluent allows higher color removals since less soluble salt is formed.

Discussion

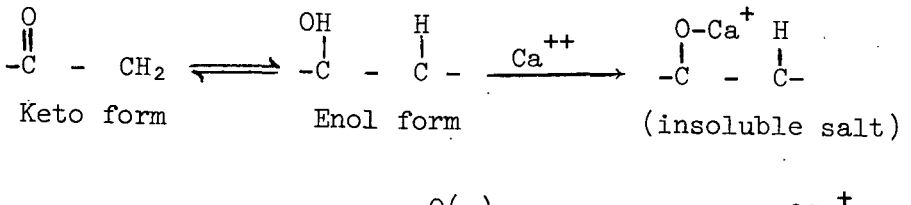
Color removal mechanism

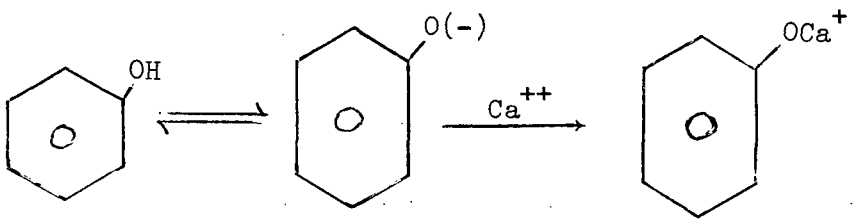
From the results of these experiments it is obvious that precipitation occurs only when the solution is highly basic and when the concen-

tration of Ca^{++} and Mg^{++} is above a critical level. Since the process depends largely on the pH, it seems reasonable to conclude that Ca^{++}/Mg^{++} reacts with the anions of dissociated weak acids rather than with weak acids themselves. Previous work (11) indicates that removal of color from spent kraft liquor by treatment with lime was not due to physical adsorption of colored material on the lime surface, but rather, was due to a chemical reaction of the chromophoric groups with lime. In the Mg^{++}/Ca^{++} process also, there is no physical phenomenon involved, but it is, apparently, purely a chemical process. The chemical phenomenon involved is best understood by considering the reaction of Mg^{++}/Ca^{++} with an acidic functional group contained in the organics in spent liquor. Carboxyl, keto/enolic, and phenolic hydroxyl groups contribute the acidic groups most likely to be encountered in the dissolved organics.

Enolic and phenolic hydroxyl groups

Ca^{++}/Mg^{++} in excess of the amount required to neutralize weakly acidic carboxyl groups were consumed in the reaction with still weaker enolic and phenolic hydroxyl groups, and in doing so caused the compounds containing such groups to precipitate as follows:





It is hypothesized that enolic and phenolic hydroxyl groups, under "alkaline conditions," react to form insoluble salts.

The need for an alkaline reaction medium implies that ionization of enolic or phenolic hydroxyl groups precedes formation of the organic salt. In regard to enolic hydroxyl groups, alkaline conditions promote displacement of the KETO-ENOL equilibrium in the direction of the enol. This explains the strong pH dependence of the Ca^{++}/Mg^{++} color removal process. At higher pH equivalent, equivalent color removal should be expected for the same dosage of calcium and magnesium.

Carboxyl group

It has been found that this acidic group is not directly involved in the color removal process. Precipitation of color bodies has been observed even after blocking carboxyl groups from reaction with bivalent ions (11).

Carboxylic acid groups contained in the effluent, however, react with calcium and magnesium to form the corresponding salts. These compounds, especially calcium salts, are thought to be soluble in water and do not contribute significantly to the color removal process. Magnesium salts, however, are typically very insoluble. This is very important and may explain why more color removal is obtained by using a Mg^{++}/Ca^{++} mixture instead of Ca^{++} alone. The amount of Mg^{++} required for acceptable color removal depends on the carboxylic content of the effluent.

Thus, it appears that the Mg^{++} dosage required for color removal is a function of the carboxylic acid group concentration present in the effluent.

If carbonate effluent contains an insignificant amount of carboxylic groups, then the addition of either Mg^{++} of Ca^{++} alone should give the same color removal at the same pH (because both Ca and Mg salts of phenolic and enolic hydroxyl groups are insoluble). If these hypotheses are correct, then the same color removal for the same dosage of bivalent metal, either Ca^{++} or Mg^{++}, should be expected at the same pH. This is indeed supported by the data given in Table III.

[Table III here]

It does not really matter whether Ca^{++} of Mg^{++} is used for the carbonate effluent because the carboxylic acid group concentration is insignificant.

Steric effect

It is thought that some of the high molecular weight phenolic or enolic compounds cannot react with Ca^{++} because of a steric effect. It was previously found (5) that because $Mg(OH)_2$ existed as a gelatinous coordinate complex, it could accept protons more readily than the lyophobic crystals of a calcium salt. This enabled the high molecular weight phenolic and enolic hydroxyl acidic group containing compounds to react with Mg^{++} and consequently precipitate. The Mg^{++} also formed less soluble organic salts over a large molecular weight range. The possibility of Mg^{++} forming a chelate complex with organic material in the solution also cannot be ruled out. However, it is believed these do not contribute much to the color removal process.

Application of model developed for Mill A effluent to Mill B effluent

The purpose of studying effluent from another "carbonate mill" was to verify the theories and model developed for Mill A effluent.

Effluent B differs physically from Effluent A in that it contains a high amount of suspended particles in the form of clay. Effluent A had color of about 1600 Pt-Co units, whereas Effluent B had a lower color content, about 870 Pt-Co units.

Table IV summarizes the results obtained when the Ca^{++}/Mg^{++} coagulation process was applied to Effluent B.

[Table IV here]

It is observed that the model works very well if only calcium is used for the coagulation process. The model does not work very well with the system containing both calcium and magnesium. The model gives a slightly erroneous prediction for a system containing only magnesium as the coagulating agent. The difference may be due to the presence of some carboxylic acid groups, or due to the presence of high molecular weight lignin compounds. A comparison of the IR spectrum for Mill A with the IR spectrum for Mill B indicated that Effluent B does contain a high proportion of carboxylic acid group compared to Effluent A. This accounts for the high percentage color removal observed in the case of the system containing only magnesium as the coagulating agent.

Thus, the model developed for Effluent A cannot be applied to any other mill's effluent, because chemical composition, turbidity and color content differ widely from one mill to another.

Conclusions

The results obtained in this work have helped in the understanding of many aspects of this coagulation process for color removal. The important conclusions derived from this work are:

1. Consistent good color removal can be obtained by using calcium alone [350 ppm at pH = 12]. It is, however, not necessary to use both calcium and magnesium as required for NSSC effluent.
2. Comparison of IR spectra of "carbonate" effluent and NSSC effluent indicate that carbonate effluent contains insignificant amounts of lignosulfates and carboxylic acid groups compared to NSSC effluent. This chemical difference could account for the role magnesium plays in such coagulation processes.
3. The color removal process is reversible and highly pH dependent. The sludge will go back into solution giving the original color if the pH is dropped to about 7.6. This fact makes raw sludge disposal inadvisable without prior incineration in order to remove color bodies so as to avoid the problem of "leaching."

Literature cited

1. Hanson, J. P., "No-sulfur Pulping Pushing out NSSC Process at Corrugating Medium Mills," Pulp Paper (March, 1978).
2. Taylor, J., "Color Removal from a Neutral Sulfite Waste Using Magnesium Coagulation," Ph.D. Thesis, University of Florida, 1976.

3. Black, A. P., Shuey, B. S., and Fleming, P. J., "Recovery of Calcium and Magnesium Values from Lime-Softening Sludges," J. Am. Water Works Assocn. 63:616 (Oct., 1971).

4. "Laboratory Studies of Magnesium Based Coagulation Process for Reduction of Color from Neutral Sulfite Effluents," National Council of the Paper Industry for Air and Stream Improvement Technical Bulletin No. 295, July, 1977.

5. Eidsness, F. A. and Black, A. P., "Carbonation of Water Softening Plant Sludge," J. Am. Water Works Assocn. 49:1343 (Oct., 1957).

6. Thompson, C. G., Singley, J. E., and Black, A. P., "Magnesium Carbonate, a Recycled Coagulant,"

   Part I. J. Am. Water Works Assocn. 64:11 (1972) — Laboratory Studies.

   Part II. J. Am. Water Works Assocn. 64:93 (1972) — Practical Application and Economic Evaluation.

7. Black, A. P., "Full Scale Studies of the Magnesium Carbonate Water Treatment Process at Montgomery, Alabama and Melbourne, Florida," EPA, Project No. 12120-HM2 (Sept., 1974).

8. Taylor, J. S., "Color Removal from Neutral Sulfite Waste Using Magnesium Coagulation," Ph.D. Thesis, University of Florida, 1976.

9. Dugal, H. S., Leekley, R. M., and Swanson, J. W., "Color Characterization Before and After Lime Treatment," EPA 660/2-74-029 (April, 1974).

10. "An Investigation of Improved Procedure for Measurement of Mill Effluent and Receiving Water Color," National Council of the Paper Industry for Air and Stream Improvement, Technical Bulletin No. 253, Dec., 1971.

11. "The Mechanisms of Color Removal in the Treatment of Pulping and Bleaching Effluents with Lime," National Council of the Paper Industry for Air and Stream Improvement Technical Bulletin No. 239, July, 1970.

I. Differences in chemical characteristics of NSSC and carbonate effluents

NSSC	Carbonate
1. Carbonate and sulfate are major inorganics present.	1. Only carbonate is present.
2. Thiosulfate present in large amounts.	2. Insignificant amount of thiosulfate present.
3. Significant amount of lignin present.	3. Less amount of lignin present.
4. Carboxylic group is very prominent.	4. Carboxylic group is insignificant compared to aromatic nuclei.
5. Significant amount of lignosulfate present.	5. Insignificant amount of lignosulfate present.

II. Major differences between the IR spectra of Mills A and B's effluent

Effluent A	Effluent B
1. A sharp peak is observed in the range of 1380 cm^{-1}, indicating presence of some hydrate or sulfate.	1. No peak is observed at 1380 cm^{-1} but a flat curve is obtained in the range of 1400 to 1450 cm^{-1}, indicating relatively low amount of hydrate or sulfate.
2. No peak is observed at 1410 or 1575 cm^{-1} indicating insignificant amount of carboxylic groups present.	2. A relatively flat spectrum in the region of 1500 to 1575 cm^{-1} indicates that it has (although negligible compared to NSSC) relatively high amounts of carboxylic groups compared to Mill A's effluent.
3. Aliphatic C-H compound band at 2600 cm^{-1} is not very prominent.	3. Very sharp peak observed at 2600 cm^{-1}, indicating high proportions of aliphatic compounds.

III. Color removal by divalent cations with low carboxylic group content in effluent

Ca^{++} (ppm)	Mg^{++} (ppm)	pH	Color removal, (%)
10	395	12.0	88
395	10	12.0	90

IV. Observations of percentage color removal as a function of different calcium and magnesium dosages at pH = 12, for Mill B

Test	Calcium (ppm)	Magnesium (ppm)	% Color removal	% Color removal predicted from model equation	Model explains 92% of color removal, thus range of acceptable data is	Is Mill A model applicable?
1	350	0	81.7	85.3	78.5- 92.1	Yes
2	0	350	93.5	75.3	69.3- 81.3	No
3	500	0	92.2	92.1	84.7- 99.5	Yes
4	0	500	91.3	77.3	71.1- 83.5	No
5	500	500	95.6	105.2	96.7-113.5	No
6	1000	0	95.6	98.5	90.6-106.4	Yes

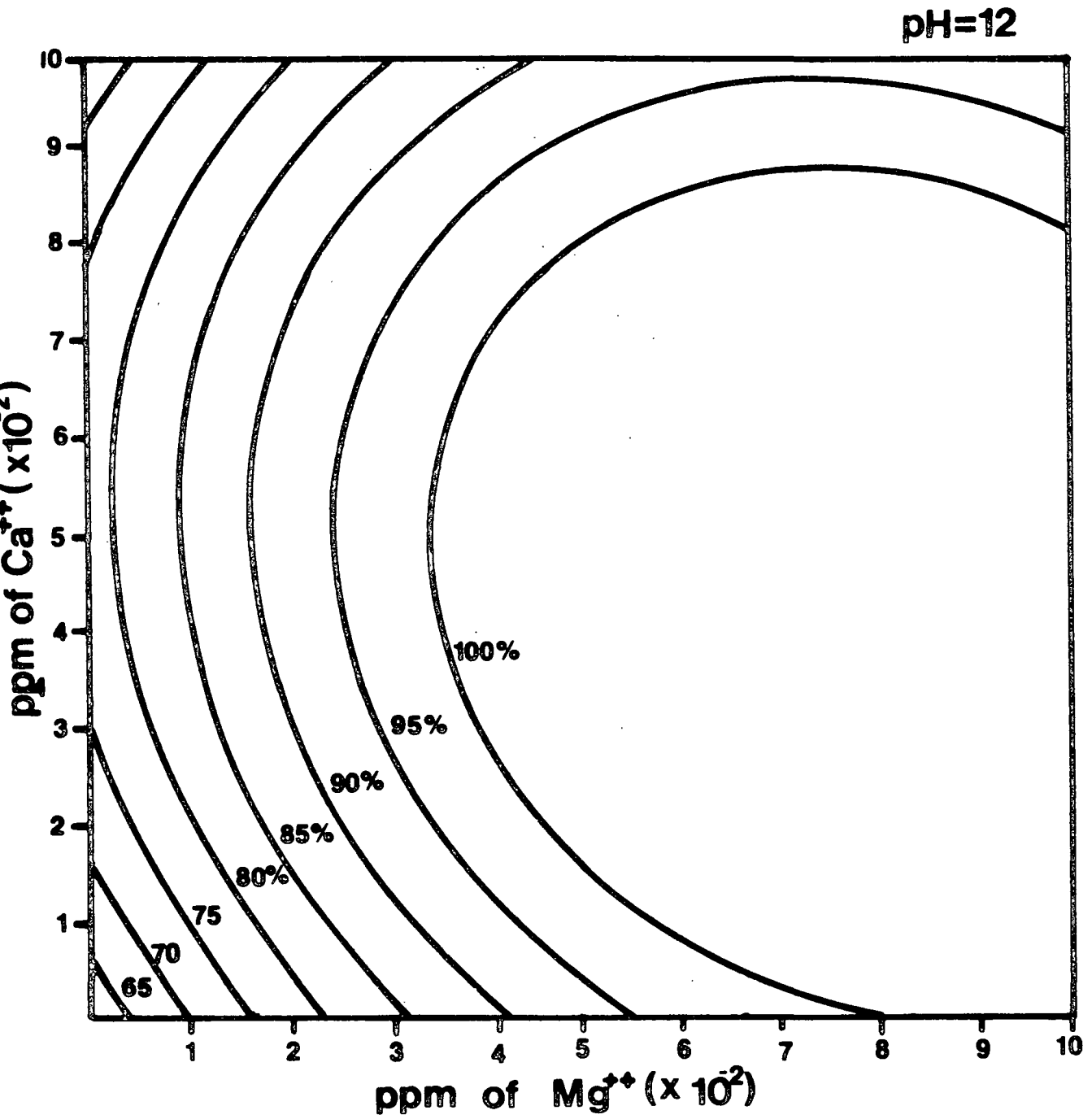


Figure 1. Percentage color removal as a function of calcium and magnesium dosage at pH = 12.

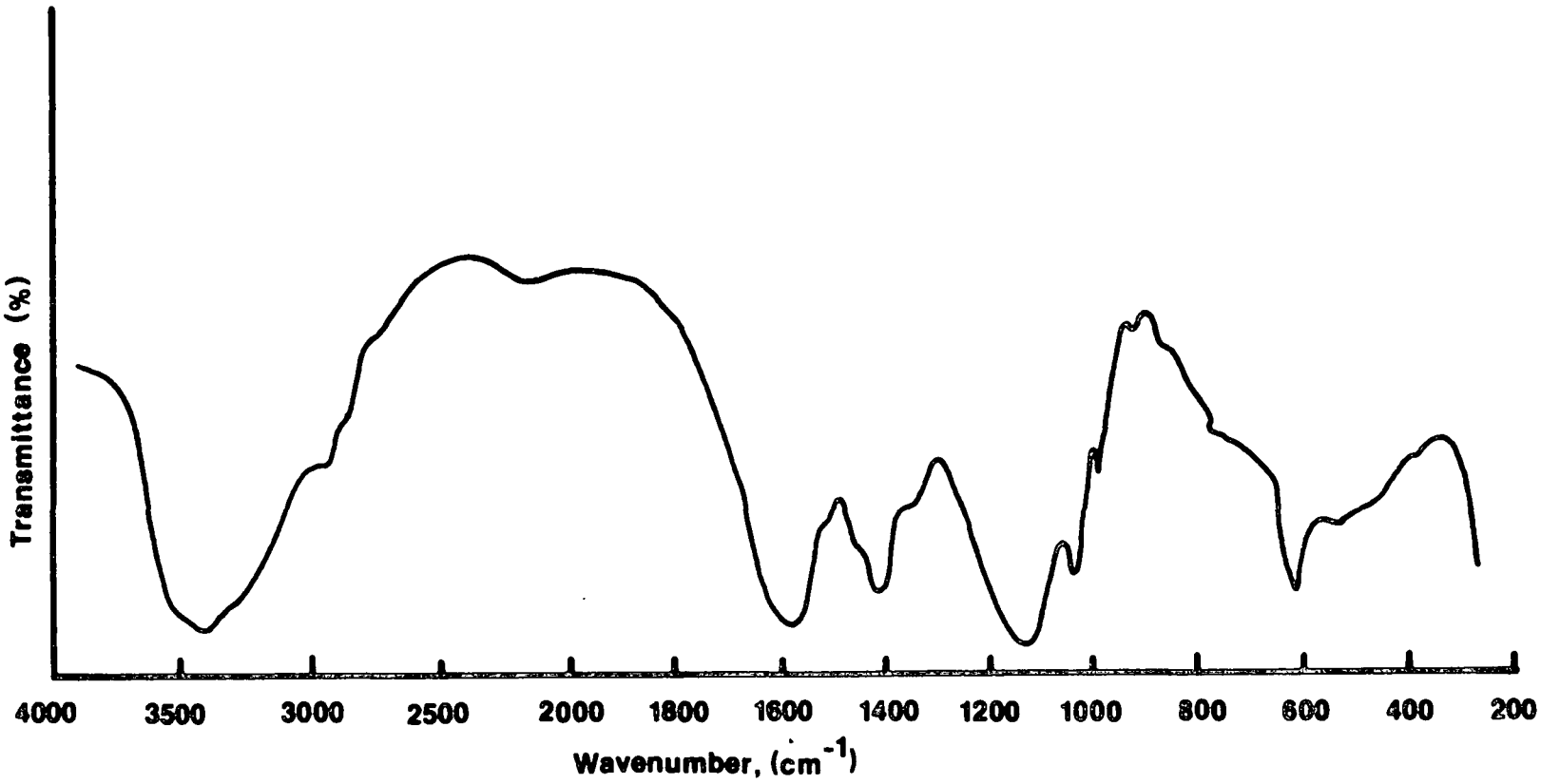


Figure 2. Neutral sulfite semichemical infrared spectra (after 5).

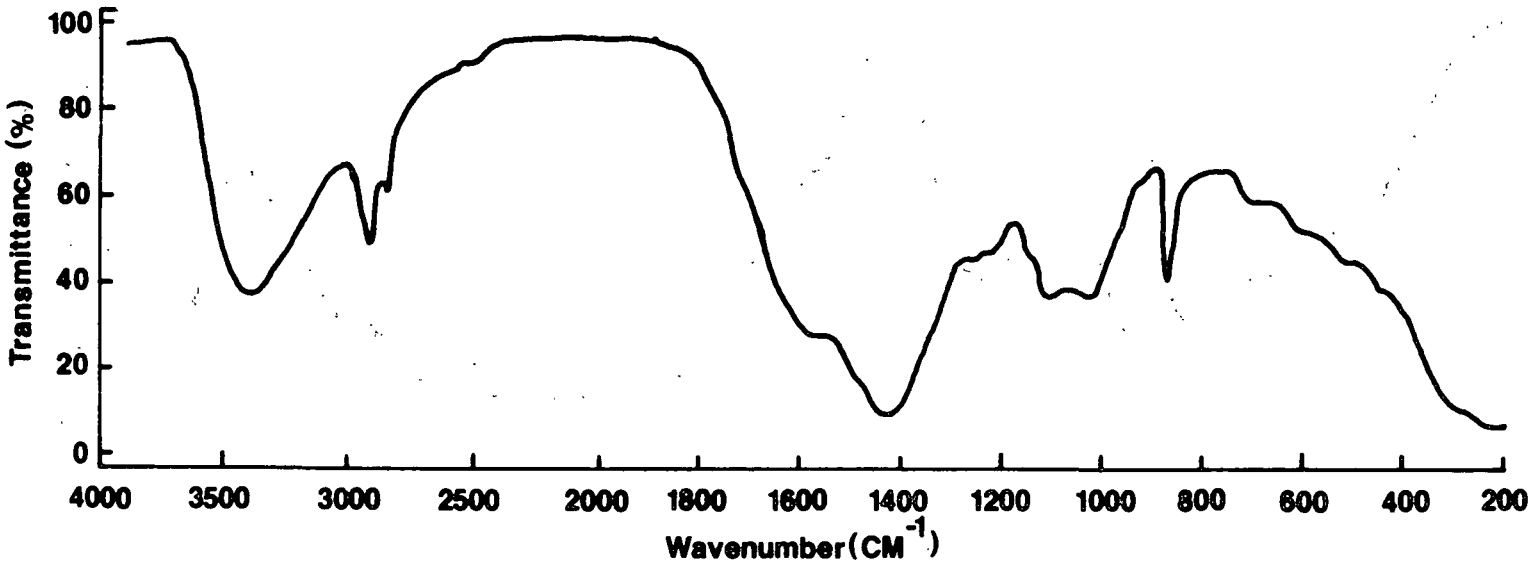


Figure 3. Infrared spectrum of untreated carbonate effluent from Mill A.

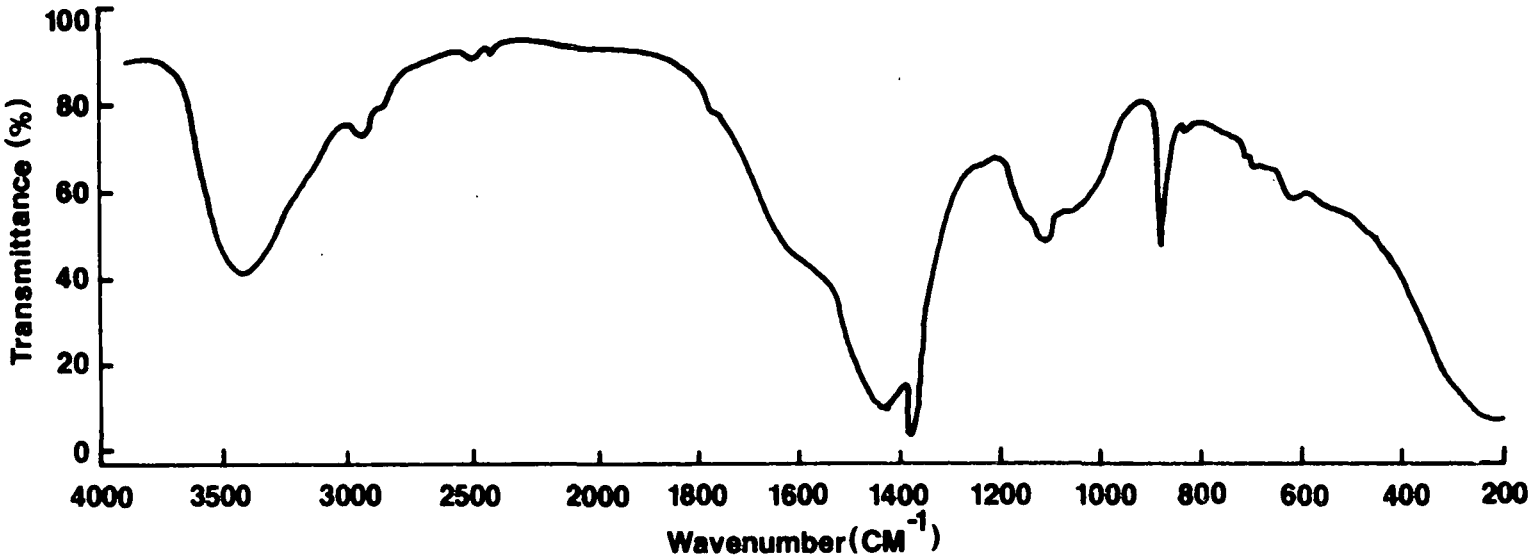


Figure 4. Infrared spectrum of untreated carbonate effluent from Mill B.